Battery500: Integrated Cell Diagnostics and Modeling to Identify Critical Gaps in Achieving High Cycle Life

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Project ID: BAT368

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STIMS #INL/CON-18-45172

Overview

Timeline

- Project start date: FY16
- Project end date: FY21
- Percent complete: 30%

Barriers

- Barriers addressed
  - Cycle Life
  - Low specific energy
  - Integrated cell design

Budget

- Total project funding: $50M
  - DOE Share:100%
  - Cost Share: 0%
- Funding for FY 2017: $10M
- Funding for FY 2018: $10M

Partners

- PNNL, INL, SLAC, Stanford, U. Washington, UT Austin, SUNY Binghamton, BNL, UC San Diego
- Project lead - PNNL

Relevance

- Ability to achieve 500 Wh/kg distinctly limited by more than just materials
  - Understanding cell design
  - Use conditions
  - Routes to enable long cycle life

FY2018 Milestones

Milestone	Status	
Q1 Establish coin cell and single layer pouch cell testing capability at INL to complement PNNL's cell fabrication's capabilities	Complete	12/31/17
Q2 Develop stage 2 coin cell and stage 1 pouch cell testing protocols.	Complete	3/31/18
Q3 Develop procedures to identify Li metal anode failure in coin cells.	In progress	6/30/18
Q4 Develop and implement methods to improve and understand cycle and calendar life limitations of pouch cells	In progress	9/30/18

Approach

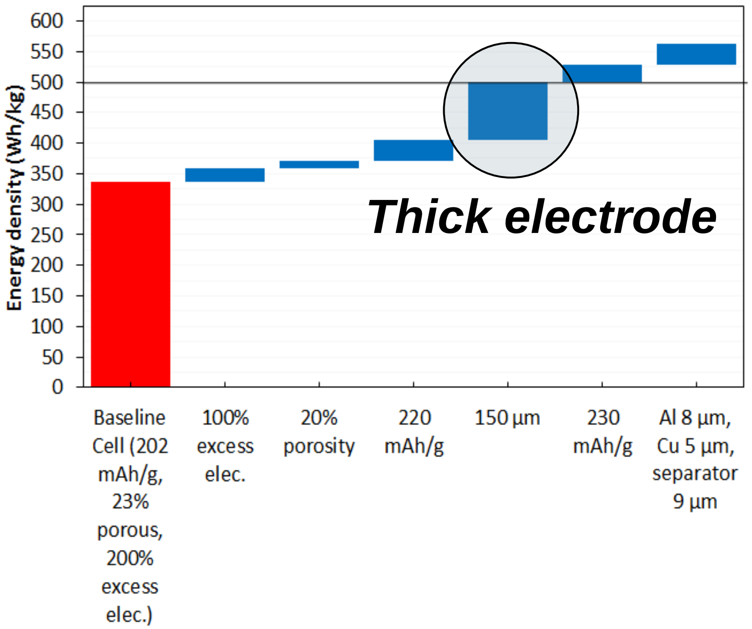
- Cell design and modeling to guide experiment, analysis and diagnostics
  - Electrode microstructure

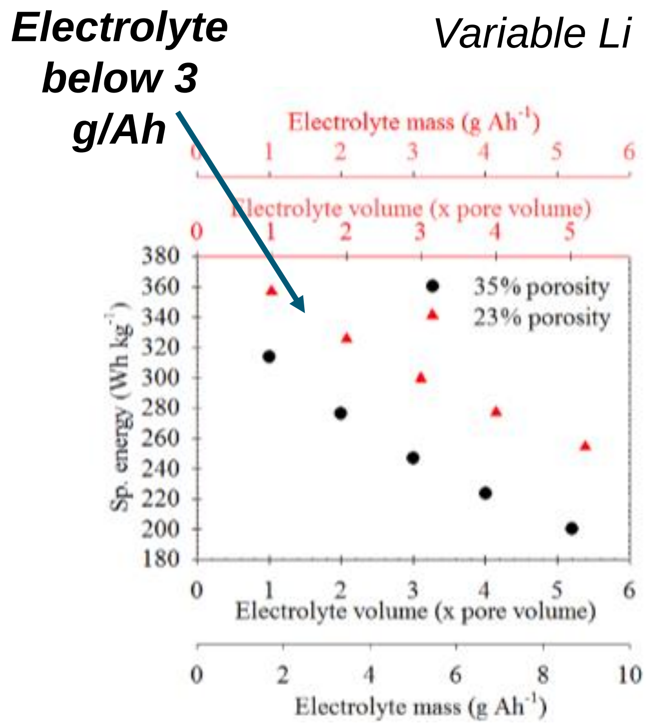
- Develop methods to quantify failure mechanism and Li transport limitations

- Identify other methods to improve cycle life (mechanical and electrical)

Technical Accomplishments
Identification of cell design limitations

(Li ‖ NMC622)
Variable electrolyte
Variable Li

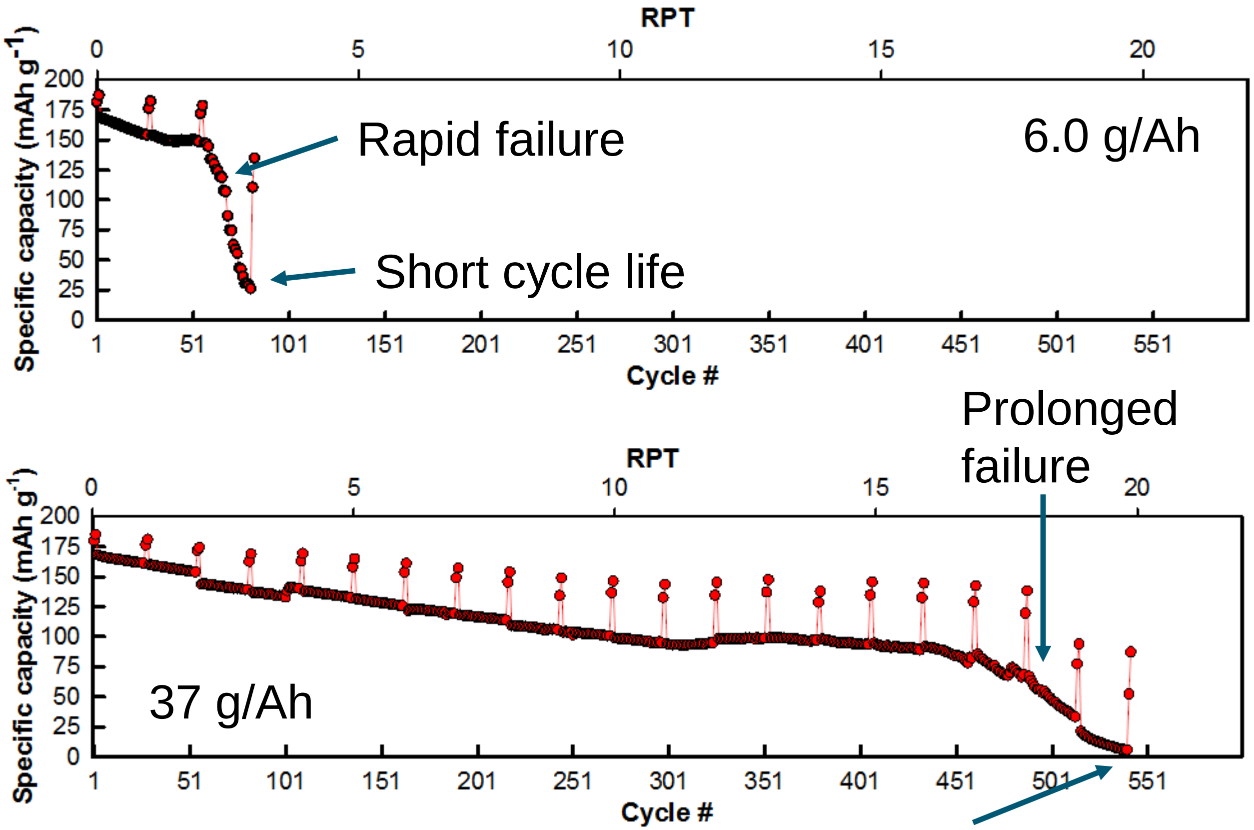




Lean electrolyte and low electrode porosity are keys to achieve high specific energy

Technical Accomplishments
Implications from reduced electrolyte

(Li ǁ NMC622)
Variable electrolyte
250 µm Li



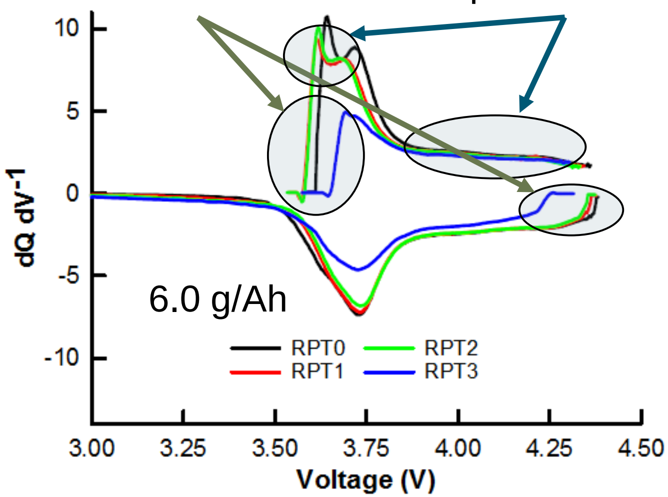
Cycling C/3, Reference performance tests (RPTs, 1 C/10, 1 C/20)

Aging path varies as electrolyte reduced

Technical Accomplishments
Identifying fade mechanisms

Sudden shift – loss of ability to transport Li in electrolyte

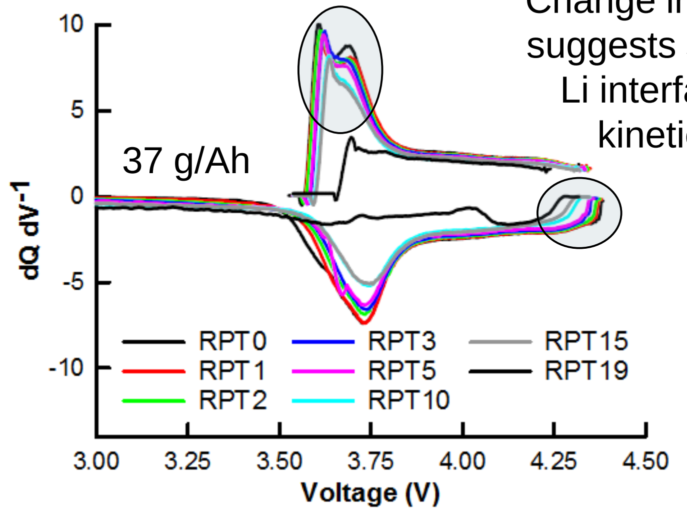
NMC retains performance



Transport limitations – Li in electrolyte

Gradual loss of cathode activity

Change in slope suggests slower Li interfacial kinetics



Transport limitations – Interface and isolation of Li

(Li ‖ NMC622)
Variable electrolyte
250 μm Li

Alignment with design enables more direct knowledge of failure

S. Nagpure et. al, submitted

Technical Accomplishment
Establishment of FY18 Testing procedures

- FY18 protocol uniform across team
- Key portions related to lean electrolyte and thin Li
- Pouch cell includes additional C/10 and C/20 cycles to quantify kinetic and thermodynamic variation

(Li ‖ NMC622)
Lean electrolyte
50 µm Li

FY18 (Stage 2) Coin Cell Testing Protocol for Li/High-Ni NMC

1. **Cathode preparation:**
   811 mixing/coating and electrode preparation process needs to be conducted inside glovebox or in dry room to minimize the exposure to air. PNNL may supply coated electrodes as baseline if needed.
   a. Requirements: areal capacity (single side): 4 mAh/cm^2
      Electrode thickness (excluding Al foil): ca.75 µm
      Press density: ca.3.0 g/cm^3
   b. Punch into disks of ½" diameter.
   c. Dry the disks in vacuum oven at 120°C for overnight.
   d. Transfer into argon-filled glovebox.

2. **Coin cell assembly:**
   a. CR2032 coin cell kits with Al-clad positive part (from MTI or other suppliers)
      Suggestion(optional): Due to the inconsistent quality of Al-clad pans, it is suggested to add one additional piece of Al foil with ¾' diameter between the cathode can and cathode to prevent corrosion of the can.
   b. HN-NMC disk, 1 piece
   c. PE separator, 20 µm thick, ¾" diameter, 1 piece
   d. Baseline electrolyte: 1.0 M $LiPF_6$ in EC-EMC (3:7 by wt.) + 2.0 wt% VC
      d1. Electrolyte amount: excessive amount of electrolyte can be used for initial evaluation of materials/electrode;
      d2. Final testing/results comparison needs to use lean electrolyte with electrolyte/capacity ratio = 3 g/Ah (for 1.27 cm^2 electrode, 0.004Ah/cm^2 x1.27cm^2 x 3g/Ah= 0.015g = 15 mg (ca.13 µL assuming ely density is 1.2g/cc)
   e. Li metal foil: 1.56 cm diameter (can start from using MTI thick Li foil) (1 piece)
      e1. Initial testing can use thick Li metal foil e.g.250 µm Li from MTI
      e2. Final testing/results comparison needs to use thin Li foil with similar cell balance design in the pouch cell e.g. ca.50 um Li (on Cu foil).
   f. SS spacer (1 piece) and SS spring (1 piece)
   g. Crimp at 1000 psi (MTI manual crimper)

3. **Testing protocols:**
   a. Testing temperature: 25°C
   b. Voltage range: 2.8 V ~ 4.4 V
   c. Resting time: 4 hrs
   d. Formation process: 2 cycles at C/10 rate (.512 mA) for charge and discharge; 1C= 4 mA/cm^2 (5.12 mA for a ½" cathode). A 1 h rest should occur between charge and discharge steps.
   e. Subsequent cycling procedure depends on your own need.

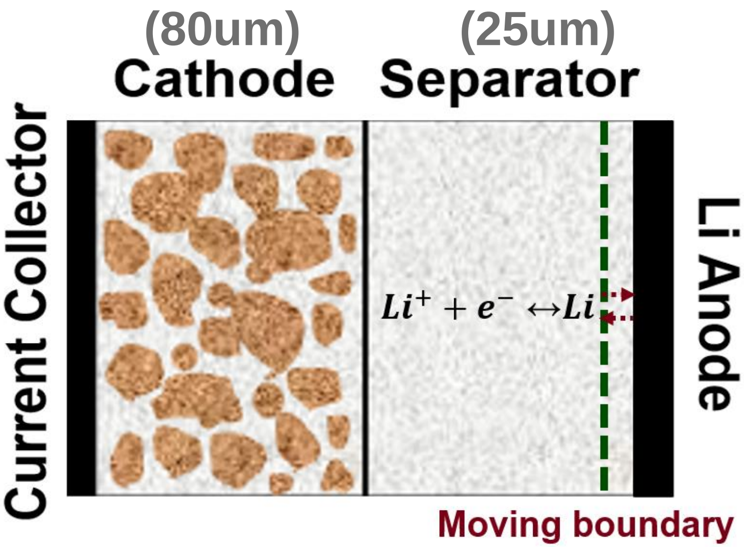
Notes:
(1) A slow deposition of Li during charge is important for stable cycling e.g., C/10 charge
(2) Optional CC-CV mode: after charging to 4.4 V, hold the cell at 4.4 V until I'=I/20. I is the current you used for charge. I' is the current below which CV mode will end. If using a CV the total length of the CV should not extend beyond 1 h even if I/20 has not been reached. The 1h maximum is mainly for safety reason especially when the cell format is increased later.

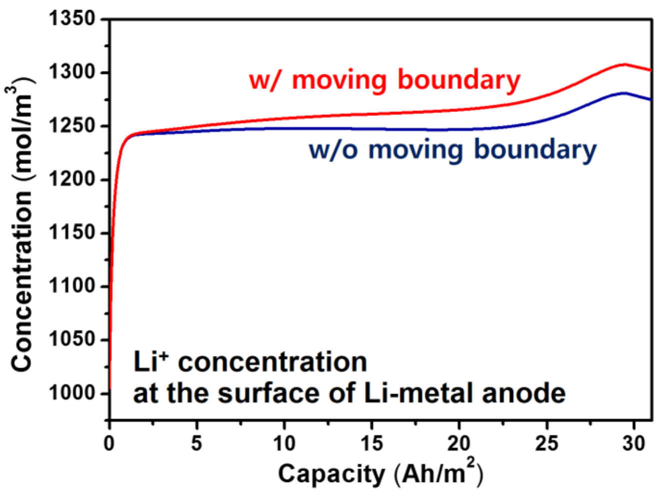
S. Chen, et. al submitted to Nat. Energy

Technical Accomplishments
1-Dimensional moving boundary with B-V kinetics

To enable moving boundary Butler-Volmer Kinetics and Corrosion components included

- Li boundary moves to simulate experiment



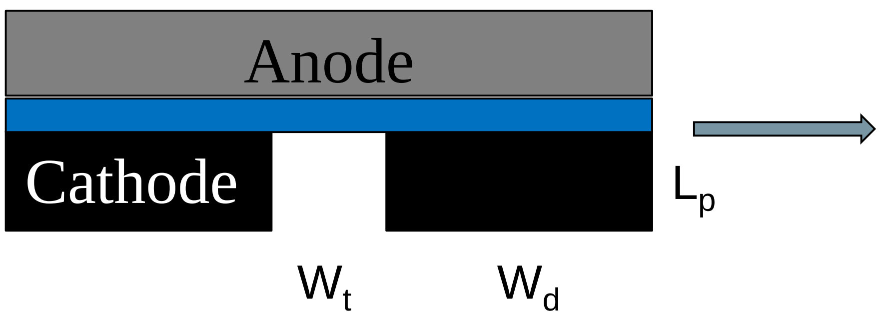


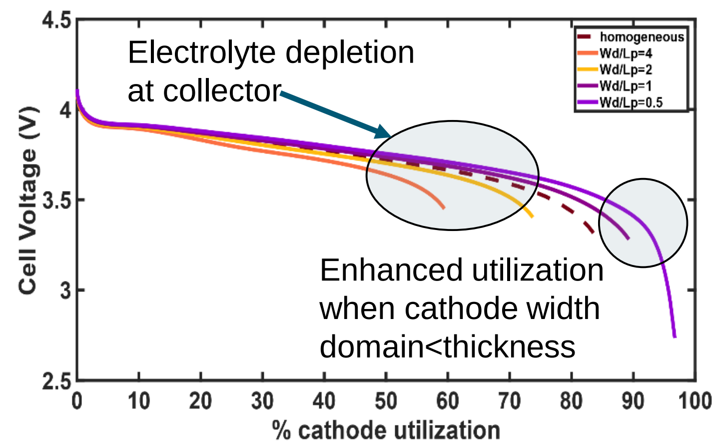
$$i_{main} = -i_0 \left(\exp\left(\alpha_c \frac{F}{RT} \eta \right) - \exp\left(-(1-\alpha_c) \frac{F}{RT} \eta \right) \right)$$

$$\eta = \phi_1 - \phi_2 - U \qquad i_{corrosion} = -i_{0,corrosion} \exp(-\alpha_c \eta) \qquad i_{main} = i_{app} + i_{corrosion}$$

Understanding surface concentration aids cell design and electrolyte development

Technical Accomplishments
Full-cell simulations of novel cathode architectures





Currently developing efficient simulation models for use as a design tool and an accessible alternative to commercial finite-element packages

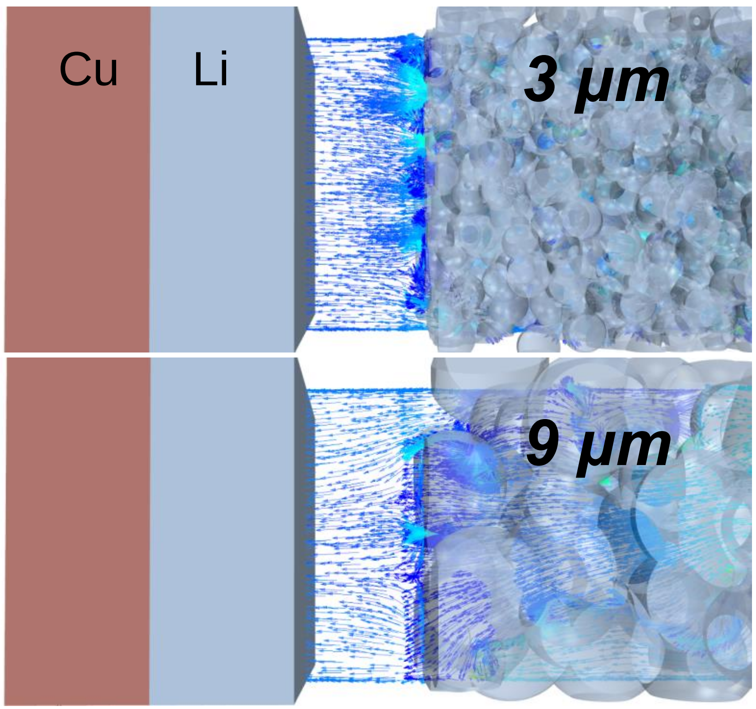
Reducing tortuosity by adding ion transport channels

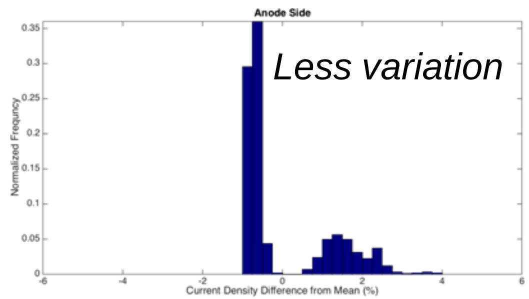
Technical Accomplishments

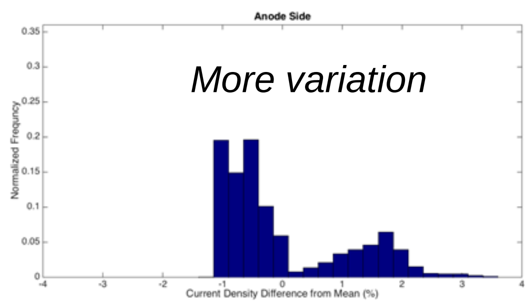
Cathode Particle Size Impacts Li

- Identifying cathode design space
  - Minimizing Li current density distribution
  - Optimizing packing density and electrode surface area

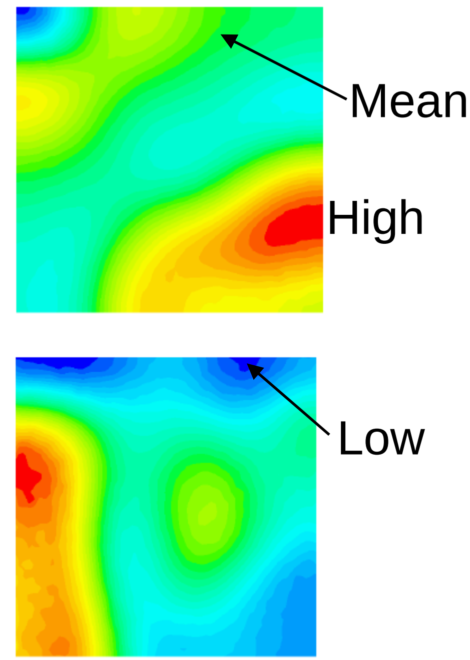
(Li ǁ NMC622)
C/10 – expected increased variation with increasing rate







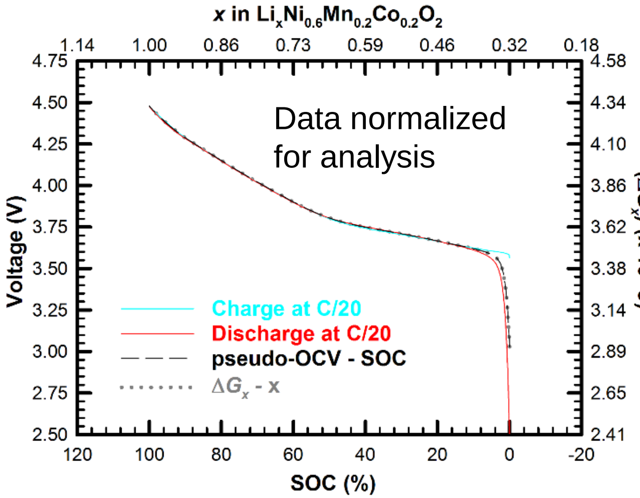
Li Current density

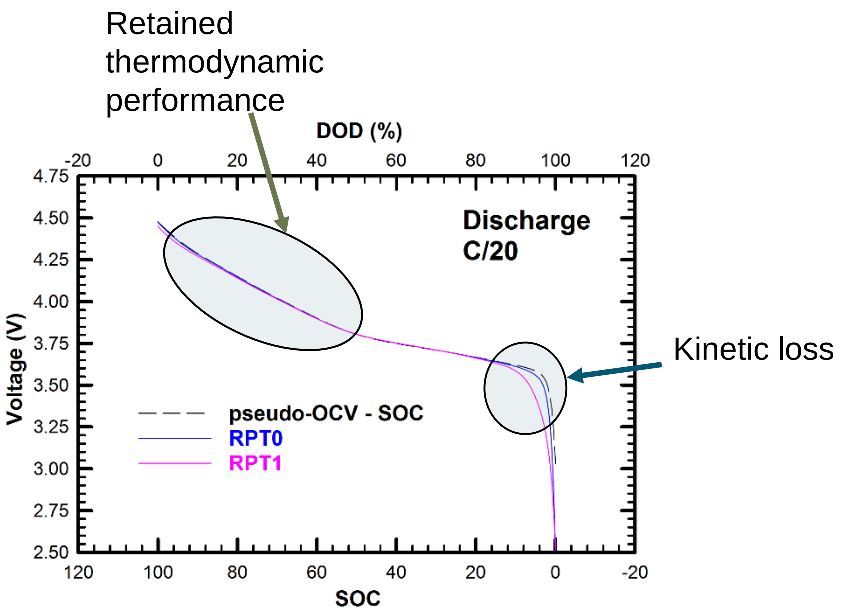


Cathode design and particle size alters field distribution at Li

Technical Accomplishments
IR Correction and SOC Adjustment

(Li ‖ NMC622)
Lean electrolyte
250 μm Li



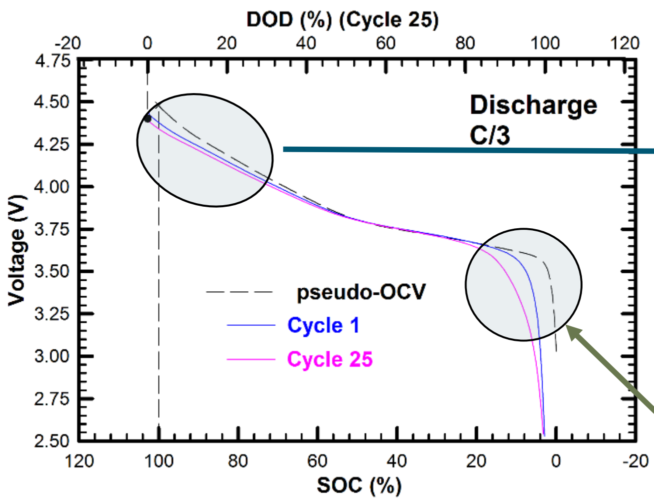


- *Information on can be directly used to aid cell design, materials development and uniform analysis across Battery500*

IR loss signify ohmic losses due to kinetic processes

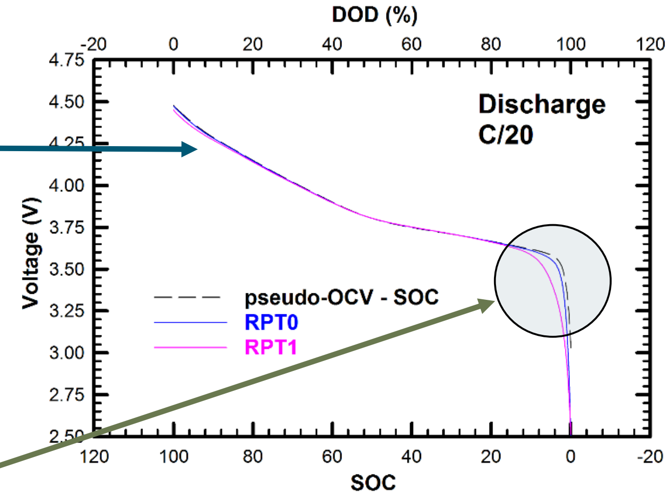
Technical Accomplishments
Assessment across cycling rates

(Li ‖ NMC622)
Lean electrolyte
250 µm Li



Design rate limitations

Aging related kinetic limitations



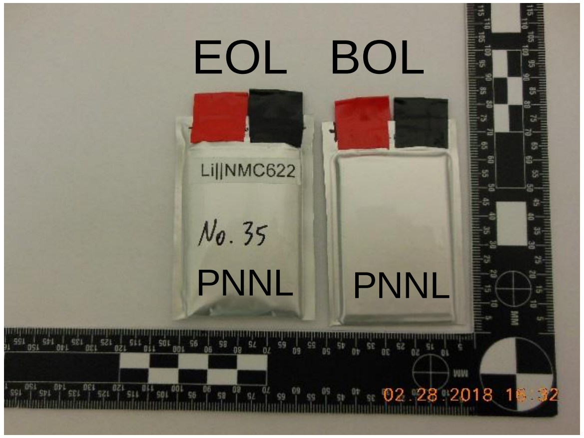
- *From thermodynamic analysis variation identified as originating from design or due to aging*

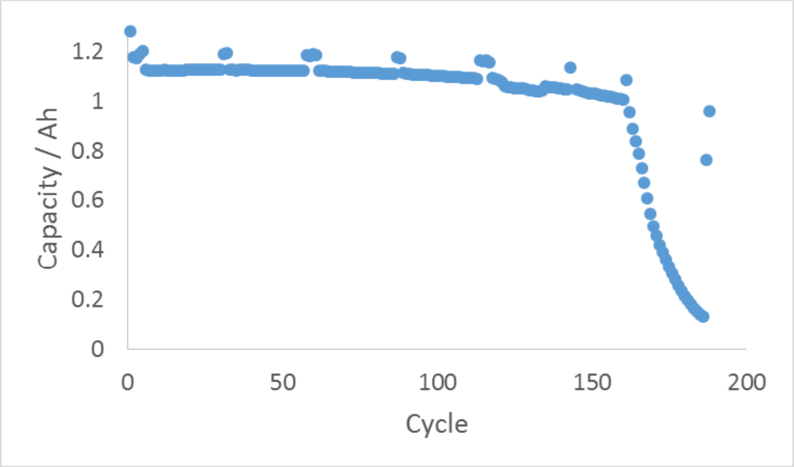
Key transport limitations can be identified and quantified

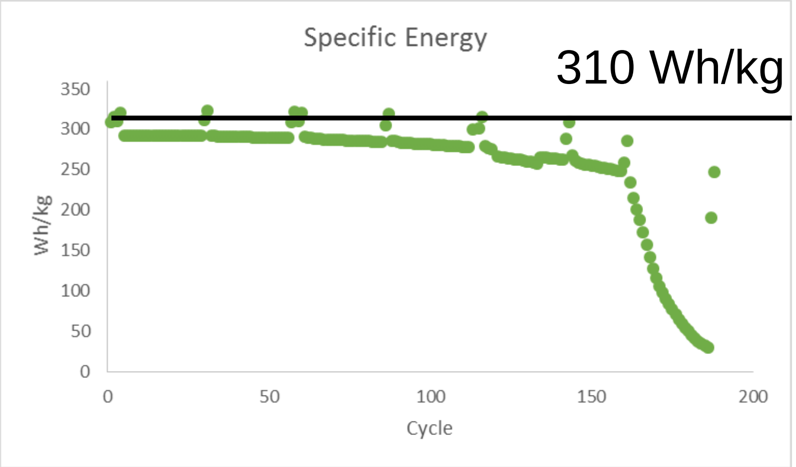
Technical Accomplishments
Pouch cell performance

- 1.15 Ah cell - 310 Wh/kg at beginning of life (C/10)
- Fixed gap, pressurized fixture (BOL)
  - Pressure maintained in realistic conditions
- Stable cycling for 160 cycles after which capacity fading is accelerated
  - Severe rate limitation near end of life (kinetic rather than thermodynamic fade)
  - Gas generation only near end of life
- Post test analysis of gas composition (H_2 and solvent)

(Li ǁ NMC622)
Lean electrolyte
50 µm Li







Responses to Previous Year Reviewers' Comments

- No reviewers comments from prior years

Collaboration and Coordination with Other Institutions

Collaboration across entire Battery500 Consortium

- PNNL (prime), INL, Stanford, SLAC, UT-Austin, U. Washington, SUNY Binghamton, UC San Diego, Brookhaven National Laboratory
  - Data and sample sharing, biweekly conference calls, quarterly meetings and joint publications
- Coordination through advisory team: USABC, IBM, FMC, Naatbatt and Tesla

Remaining Challenges and Barriers

- Maintaining cyclability for high specific energy designs
  - Jointly understanding performance and safety
  - Uncertain calendar life for high energy designs
- Continued refinement of fade mechanisms associated with Li-S and Li-NMC
- Computationally-guided cell design refinement which minimizes inactive components
  - Variability and the role that inhomogeneity plays in fade/failure

Proposed Future Research

FY2018

- Identify Li metal failure and the impacts of non-material cell influence e.g. external pressure
  - Coordination of experimental full cell work and advanced diagnostics at SLAC, BNL, etc.
- Enhance understanding on root causes of pouch and coin cell failure when using realistic cell design parameters
- Further coordinate model efforts with the introduction of new materials and designs into coin and pouch architectures

FY2019

- Extend analysis methods to Li-S chemistry and cell designs

Any proposed future work is subject to change based on funding levels

Summary

- Distinct approach to standard procedures which provides uniformity in evaluation and enables robust analysis
- Analysis methods in place to more directly correlate fade across program
- Specific modeling activities to focus on core areas for extending life and specific energy